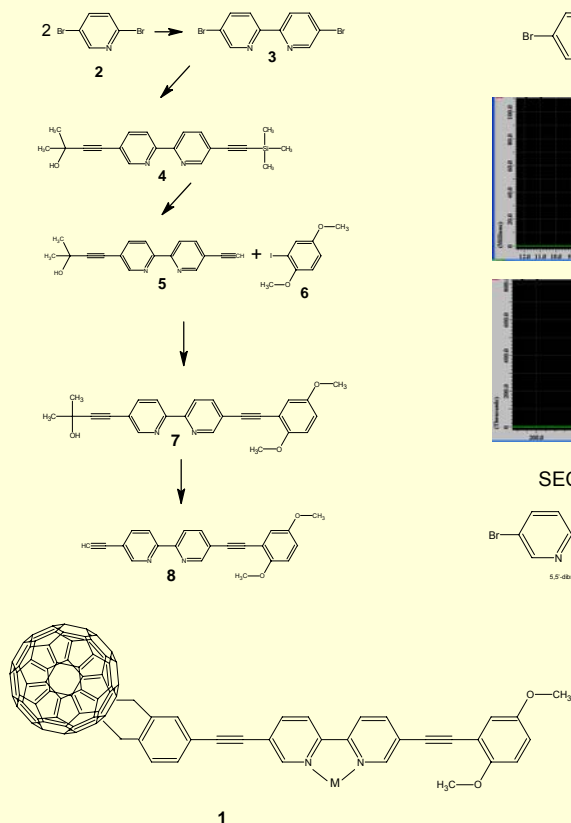


James Kareth, Tiffany Tanner, Keith A. Walters

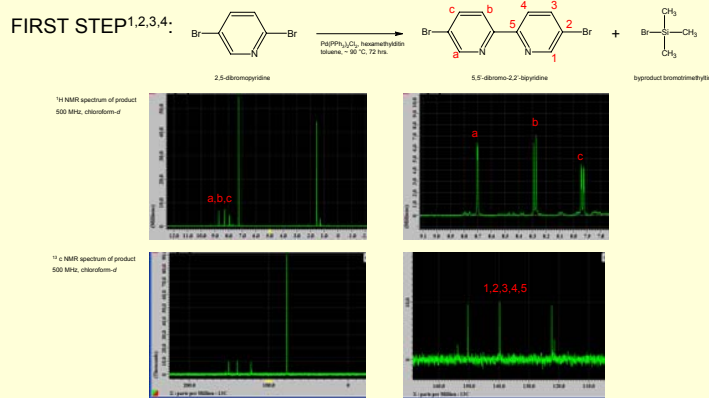
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**ABSTRACT:** Supramolecular complexes consisting of fullerenes bonded to bipyridines coordinated with transition metal atoms can absorb a photon of light, causing an electron in the fullerene to transition to a higher energy level. The excited electron transfers through the bipyridine to the coordinated metal atom and then out of the complex. These complexes are useful in charge transfer applications, such as solar cells, light emitting diodes (LEDs) and molecular wires. These complexes are typically symmetrical, with one fullerene on each side of the bipyridine. Fullerenes are insoluble in most solvents. Thus, in situations where the complex must function in solution, it is anticipated that asymmetric complexes containing only one fullerene bonded to one side of the bipyridine are necessary to allow the complex to dissolve in solution. Asymmetric complexes, however, are more difficult to synthesize than symmetric complexes. This research concerns the synthesis of asymmetric fullerene bipyridine transition metal complexes.

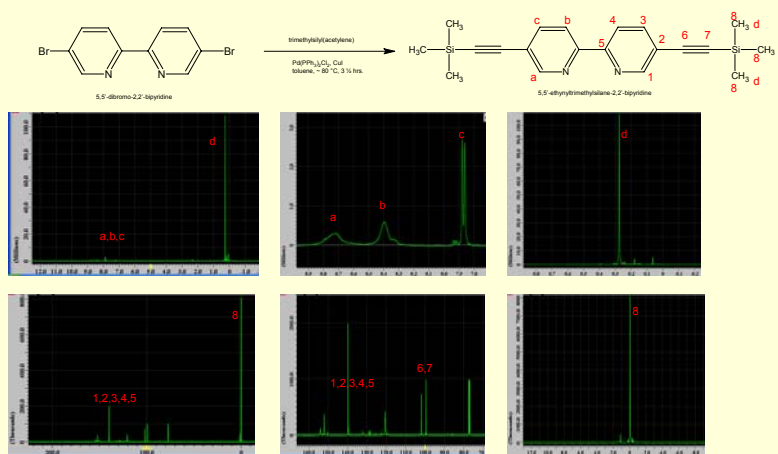
**PURPOSE:** The purpose of this research is to develop a five step process to synthesize 5-ethyne-5'-ethynyl(2,5)dimethoxybenzyl-2,2'-bipyridine **8**. The first step uses the readily available starting material 2,5-dibromopyridine **2** to form 5,5'-dibromo-2,2'-bipyridine **3**. In the second step, the 5-bromine of **3** is substituted with an ethynyl dimethylpropargyl alcohol group and the 5'-bromine of **3** is substituted with an ethynyl trimethylsilyl group to form 5-ethynyl(2,5)dimethoxybenzyl-5'-ethynyltrimethylsilyl-2,2'-bipyridine **4**. In the third step, the trimethylsilyl group is removed from the ethyne group of **4** to form 5-ethynylpropargyl-5'-ethyne-2,2'-bipyridine **5**. In the fourth step, the hydrogen on the 5'-ethyne group of **5** is substituted with a dimethoxy benzene capping group **6** to form 5-ethynylpropargyl-5'-ethynyl(2,5)dimethoxybenzyl-2,2'-bipyridine **7**. In the fifth step, the dimethylpropargyl alcohol group of **7** is removed to form 5-ethyne-5'-ethynyl(2,5)dimethoxybenzyl-2,2'-bipyridine **8**. Future research will be conducted to substitute the hydrogen of the 5-ethyne group of **8** to a previously prepared substituted fullerene using the Sonogashira coupling reaction to form an asymmetric fullerene bipyridine macromolecule, which will then be coordinated to a transition metal to form the asymmetric fullerene bipyridine transition metal complex **1**.



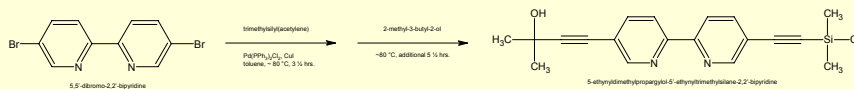
FIRST STEP 1,2,3,4:



TEST METHODOLOGY FOR SECOND STEP<sup>5</sup>:



SECOND STEP 4<sup>5</sup>:



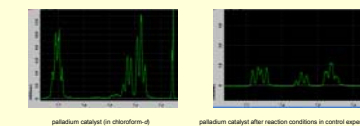
The second step has not progressed sufficiently to provide suitable NMR results.

POTENTIAL INTERFERENCE WITH SYNTHESIS

Initial attempts to synthesize 5-ethynyl(2,5)dimethoxybenzyl-5'-ethynyltrimethylsilyl-2,2'-bipyridine (Step 2) produced a black, sticky, tar like substance. While traces of the desired product were detected in the reaction mixture, the product could not be separated from the tar substance. Several potential causes of the tar substance were considered, and the methodology was eventually changed to eliminate the problem. Each potential interference is examined as follows.

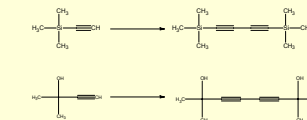
### 1. Palladium catalyst decomposition and 2° vs. 3° amine

Step 2 was initially performed using a secondary amine (*n*-propylamine) as the Lewis Base. Secondary amines have been known to cause decomposition of palladium / triphenylphosphine catalysts (bis and tetrakis) under certain conditions, and tertiary amines have been used as the Lewis Base instead to prevent the decomposition.<sup>5</sup> A series of control reactions using *n*-propylamine and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> produced a black powder, indicating possible decomposition of the catalyst. Triethylamine was substituted for *n*-propylamine in Step 2 and the tar substance was no longer present in the reaction mixture.



### 2. Homocoupling of substituted acetylene reagents

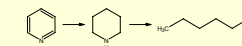
Substituted acetylene reagents (such as the trimethylsilyl(acetylene) and 2-methyl-3-butyl-2-ol) used in Step 2) have been known to homocouple under reaction conditions similar to those used in Step 2.<sup>6,7</sup>



The acetylene chains of homocoupled substituted acetylenes were considered as potential causes of the tar substance. Micro syringes were used to add the substituted acetylene reagents to the reaction in an attempt to reduce the amount of excess reagent available for homocoupling, and the tar substance no longer present in the reaction mixture.

### 3. Hydrodenitrogenation of pyridine

Hydrodenitrogenation is a process where a proton is added to the nitrogen in pyridine causing the pyridine ring to cleave and form an alkyl chain under certain reaction conditions.<sup>8</sup> This process is commonly used to remove nitrogen from petroleum feedstocks.



The possibility of cleaved bipyridines forming complex alkyl chains was considered as a potential cause of the tar substance, but literature research indicated<sup>8</sup> that the reaction conditions used in Step 2 were not sufficient to cause hydrodenitrogenation.

**ACKNOWLEDGEMENTS:** This research was funded by Northern Kentucky University, the Chemistry Department of Northern Kentucky University, and CINSAM. Sincere appreciation is expressed for this financial support.

### REFERENCES:

1. Bruce, J.I.; Chambron, J.C.; Koller, P.; Sauvage, J.P., Synthesis of a linear bis-porphyrin with a Ru(phen)22+ -complexed 2,2'-bipyridine spacer. *J. Chem. Soc., Perkin Trans. 1*, **2002**, 1226-1231.
2. Schubert, U.S.; Eschbaumer, C.; Heller, M., Stille-Type Cross-Coupling – An Efficient Way to Various Symmetrically and Unsymmetrically Substituted Methyl-Bipyridines: Toward New ATRP Catalysts. *Organic Letters*, **2000**, 2 (21), 3373-3376.
3. Opris, D.M.; Franke, P.; Schluter, A.D., Shape-Persistent Macrocycles with Bipyridine Units: Progress in Accessibility and Widening of Applicability. *Eur. J. Org. Chem.*, **2005**, 822-837.
4. Ley, K.D.; Li, Y.; Johnson, J.V.; Powell, D.H.; Schanze, K.S., Synthesis and characterization of  $\pi$ -conjugated oligomers that contain metal-to-ligand charge transfer chromophores. *Chem. Commun.*, **1999**, 1749-1750.
5. Klyatskaya, S.V.; Tretyakov, E.V.; Vasilievsky, S.F., Synthesis and chemical properties of polyacetylenic derivatives of benzo- and dibenzo- crown ethers. *ARKAT-USA Jour.*, **2003**, 13.
6. Li, J.H.; Liang, Y.; Xie, Y.X., Efficient Palladium-Catalyzed Homocoupling Reaction and Sonogashira Cross-Coupling Reaction of Terminal Alkynes under Aerobic Conditions. *J. Org. Chem.*, **2005**, 70, 4393-4396.
7. Lei, A.; Srivastava, M.; Zhang, X., Transmetalation of Palladium Enolate and Its Application in Palladium-Catalyzed Homocoupling of Alkynes: A Room-Temperature, Highly Efficient Route to Make Dienes. *J. Org. Chem.*, **2002**, 67, 1969-1971.
8. Bianchini, C.; Mei, A.; Vizza, F., Modelling the Hydrodenitrogenation of Aromatic N-Heterocycles in the Homogeneous Phase. *Eur. J. Inorg. Chem.*, **2001**, 43-68.